



# ***Non-Precious Metal Electrocatalysts***

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## ***Argonne National Laboratory***



A U.S. Department of Energy  
Office of Science Laboratory  
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# ***Project objective***

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- **Develop a non-precious metal cathode electrocatalyst for polymer electrolyte fuel cells**
  - Promotes the direct four-electron transfer with high electrocatalytic activity (comparable to that of Pt)
    - *O<sub>2</sub> reduction reaction (ORR) in acidic media (e.g, in PEFC)*
      - *Two-electron transfer*
$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$$
      - *Four-electron transfer*
$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2 \text{H}_2\text{O}$$
      - *Four-electron process is desirable due to its higher efficiency and non-corrosive product*
    - Chemically compatible with the acidic polymer electrolyte
    - Low cost

# ***Budget – New FY'04 Project***

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- FY'04 Funding: \$300 K

# ***Technical Barriers and Targets***

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- **This project addresses DOE's Technical Barriers for Fuel Cell Components**
  - O: Stack Material and Manufacturing Cost
  - P: Component Durability
  - Q: Electrode Performance
- **DOE's Technical Targets:**
  - Low cost, <\$5/kW
  - Durability, >5,000 operating hours

# Approaches

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- **Complex oxides containing transition metals with multiple oxidation states (e.g., spinels and perovskites)**
  - Oxides of metals with multiple oxidation states (e.g., Co, Ni, Fe, Mn) contain oxygen vacancies or defects that may facilitate oxygen binding and dissociation
  - Host oxide is chosen to be stable in the acidic environment (e.g., titanium and chromium oxide)
- **Transition metal carbides and nitrides**
  - Contain surface vacancies and defects
  - Isoelectronic with platinum (e.g., WC), catalytically active in hydro-treating and dehydration reactions
  - Resistant to acidic corrosion and electronically conducting
- **Metal centers attached to an electron-conducting polymer backbone**
  - Allows easy control of spacing between metal centers
  - Electron conductor in close proximity to reaction site can promote high catalyst utilization

# Safety

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- **Internal safety reviews have been performed for all aspects of this project to address ESH issues**
  - Electrocatalyst and electrocatalyst/electrolyte ink synthesis
    - *All synthesis is performed in a hood to exhaust vapors of organic solvents and to prevent dust inhalation*
    - *Used electrocatalysts and inks are collected and disposed of through the laboratory's Waste Management Operations*
  - Electrocatalyst testing
    - *Purge gas is either inert Argon or Oxygen*
- **Safety reviews are updated and renewed annually**

# Project timeline

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FY'04				FY'05	
1	2	3	4	5	6

- 1: Establish and verify test procedure✓
- 2: Identify one or more potential cathode electrocatalysts✓
- 3: Determine kinetics and stability of potential electrocatalysts✓
- 4: Begin first principles calculations, quantum chemical modeling to guide selection of potential electrocatalysts
- 5: Refine choice of electrocatalysts based on modeling and experimental work and evaluate these catalysts
- 6: Fabricate and evaluate a membrane-electrode assembly using newly-developed cathode electrocatalyst

# ***A rotating ring-disk electrode apparatus is being used to evaluate ORR kinetics***

## ● **Electrocatalyst preparation**

- Mix powdered electrocatalyst with 5 wt% solution of polymer electrolyte (Nafion®) to form an ink
- Vulcan XC72 carbon is added to ink if material is not an electron conductor
- Ink supported on a glassy carbon rotating disk electrode (RDE)

## ● **Electrochemical measurements (23°C)**

- RDE/thin film technique allows one to eliminate the effects of mass transfer
- Platinum ring electrode will be used to detect intermediates (e.g.,  $\text{H}_2\text{O}_2$ )
- Background voltammograms in deaerated 0.5 M  $\text{H}_2\text{SO}_4$  to determine material stability
- Steady-state voltammograms in  $\text{O}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  at various rotation rates to determine kinetics of ORR





# ***The kinetics of the oxygen reduction reaction (ORR) were determined on Pt/C to verify the RDE technique***

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- **Electrocatalyst**

- 20 wt% Pt on Vulcan XC-72 (E-TEK)
- Mixed with 5 wt% of polymer electrolyte (Nafion<sup>®</sup>) to form an ink with Pt/C : Nafion = 60:40
- Ink supported on a glassy carbon rotating disk electrode (RDE)

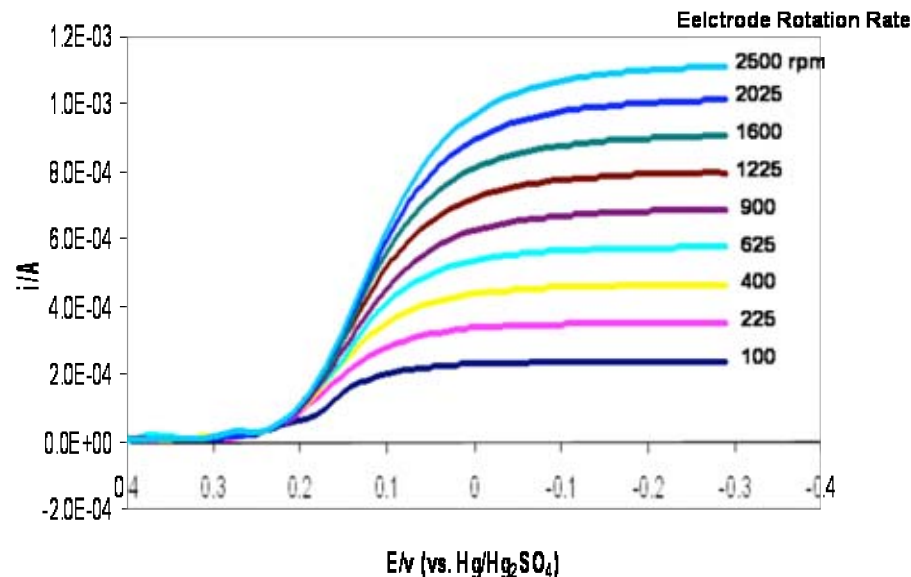
- **Electrochemical measurements (23°C)**

- In Ar-deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub>
  - *Used to determine the electrochemically active surface area of Pt from hydrogen adsorption/desorption peaks in the cyclic voltammogram*
  - *Background voltammograms at various rotation rates*
- In O<sub>2</sub>-saturated 0.5 M H<sub>2</sub>SO<sub>4</sub>
  - *Steady-state voltammograms of the ORR at various rotation rates*

# Levich-Koutecky equation used to extract kinetic current from steady-state voltammograms

- Steady-state voltammograms of the ORR on Pt/C/Nafion® on a glassy carbon RDE

Equation	Electrode Type
Levich-Koutecky equation $\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{K\omega^{1/2}}$	Smooth electrode
Kinetic current derived from Levich-Koutecky equation $i_k = \frac{i_d \cdot i}{i_d - i}$	Smooth electrode
Extended Levich-Koutecky equation $\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_f} + \frac{1}{i_d} = \frac{1}{i_k} + \frac{1}{i_f} + \frac{1}{K\omega^{1/2}}$	Thin film electrode



- Three methods were used to determine the ORR kinetic current from the RDE experiments on Pt/C

# ***Tafel plots were used to extract kinetic parameters for the ORR on Pt/C/Nafion<sup>®</sup>***

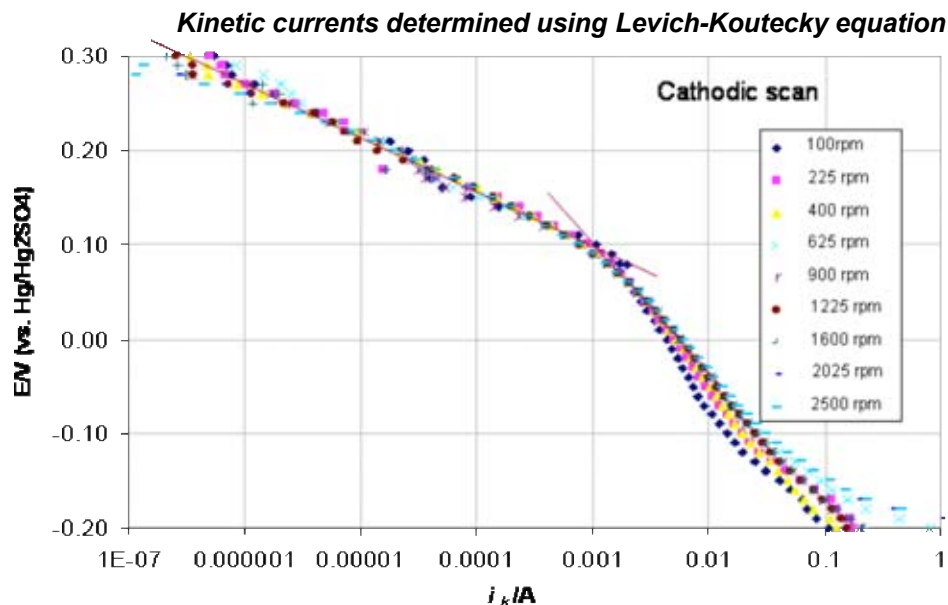
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- **Tafel plot**  $\eta = \frac{RT}{\alpha n F} \ln i_o - \frac{RT}{\alpha n F} \ln i, \quad \eta = E - E_{eq}$
- **Tafel-like plot**  $E = E_{eq} + \frac{RT}{\alpha n F} \ln i_o - \frac{RT}{\alpha n F} \ln i$
- **A plot of  $E$  vs.  $\ln i$  should give a straight line with**

$$\text{Slope} = -\frac{RT}{\alpha n F}, \quad \text{Intercept} = E_{eq} + \frac{RT}{\alpha n F} \ln i_o$$

$i_o$ : exchange current density,  $\alpha$ : transfer coefficient

# Tafel slopes for the ORR on Pt/C/Nafion<sup>®</sup> agree well with literature values



**Tafel plot of ORR on Pt/C electrode has high and low slope regions**

Method to obtain $i_k$		Negative scan direction		Positive scan direction		
		Tafel slope (mV/dec)		Tafel slope (mV/dec)		
(id · i)/(id – i)	Average of all rotation rates	low i	high i	low i	high i	
		-58	-127	-82	-124	
Levich-Koutecky		-77	-134	-86	-134	
Extended Levich-Koutecky		-73	-130	-86	-136	
Martin (1992) Microelectrode Pt	30°C, 5 atm	-65	-123			
	50°C, 1.1 atm	-71	-130			
Gojkovic (1998) Pt/C/Nafion mixture, 25°C		-60		-80		
Paulus (2001) Pt/C/Nafion film, 20°C				-63	-120	

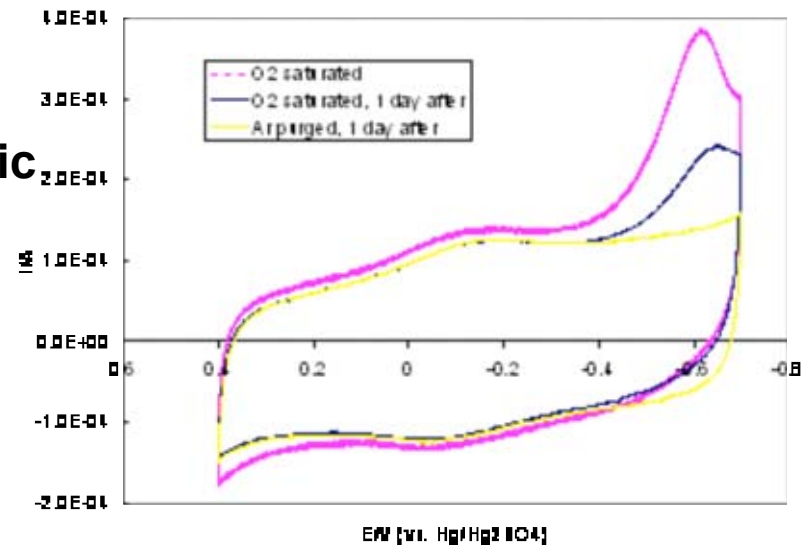
# ***Exchange current density for the ORR on Pt/C/Nafion<sup>®</sup> agrees with literature values***

Temperature (°C)	$i_o$ (A/cm <sup>2</sup> )				Remarks
	Negative scan		Positive scan		
	low $i$	high $i$	low $i$	high $i$	
23	4.6 x 10 <sup>-11</sup>	9.3 x 10 <sup>-8</sup>	1.0 x 10 <sup>-9</sup>	9.4 x 10 <sup>-8</sup>	This work Averaged for 100 ~ 2500 rpm
30	1.7 x 10 <sup>-10</sup>	2.8 x 10 <sup>-7</sup>			Martin (1992) Pt microelectrode Po <sub>2</sub> = 5 atm
40	7.3 x 10 <sup>-10</sup>	3.2 x 10 <sup>-7</sup>			
40	2.0 x 10 <sup>-9</sup>				Appleby (1993) 20 wt% Pt/C in a full cell
95	3.1 x 10 <sup>-9</sup>				

# Progress on testing candidate materials

Oxides	Milling	Oxide to Carbon Ratio (wt%)			Composite to Nafion Ratio (vol%)
Co-Cr-O	Wet, 16h	20:80	50:50	80:20	50:50
Ni-Cr-O	“	20:80	50:50	80:20	62:38
Fe(III)-Ti-O	Dry, 16h	20:80			64:36
Fe(II)-Ti-O	Wet, 9h	50:50	80:20		40:60
Fe(III)-Ti-O	No milling	75:25			40:60
Ce-W-O	“	65:35	85:15		40:60
Ce-V-O	No milling	80:20			40:60

- **Voltammetry of Ni-Cr-O/Carbon/Nafion showed ORR activity, but instability in acidic environment**
- **Other complex oxides showed either no ORR activity or instability in acid**
- **Beginning testing of carbides and nitrides**



## ***Future work – FY'04 and beyond***

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- Investigate methods for stabilizing complex transition metal oxides
- Test the ORR activity of select transition metal carbides and nitrides
- Begin synthesis of metal centers attached to polymer backbones
- Incorporate higher temperature ORR kinetic measurements when a high-temperature RDE becomes available
- Begin theoretical work (e.g., DFT calculations) to guide choice of candidate materials
- Fabricate and test a membrane-electrode assembly using newly-developed cathode electrocatalyst



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